New Aminoethylsulfanyl-Substituted Tribenzoporphyrazines

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Summary. Unsymmetrical metal-free and metalo-porphyrazines ($M = $ Mg, Zn, Co) made up of three phthalonitrile units and a single maleonitrile moiety on the periphery were prepared by cyclization of bis(2-dimethylaminoethylthio)maleonitrile and phthalonitrile. The magnesium derivative (Mgpz) was converted into the quaternized product by reaction with methyl iodide. The new compounds were characterized by elemental analysis, IR, NMR, mass, and electronic spectra.

Keywords. Dithiamaleonitrile; Porphyrazines; Magnesium; Cobalt; Zinc.

Introduction

Tetrapyrrolic macrocycles, such as porphyrines and phthalocyanines or their aza anologues, are the object of extensive studies for several decades and their practical applications have been even investigated more intensively during the last years [1, 2]. These macrocycles have found wide applications in areas, such as biomedical agents for diagnosis and therapy, chemical sensors, liquid crystals, non-linear optics, photovoltaic cells, optical limiting agents, *Langmuir-Blodgett* films, and ladder polymers, and are precursors to new conducting materials in addition to their traditional use as dyes and pigments [2–9].

Considering that a tetraazaporphyrin molecule is a hybrid of porphyrin and phthalocyanine, it is not unexpected that the chemical and physical properties of tetraazaporphyrins lie somewhere between those of phthalocyanine and porphyrins. Porphyrazines and related molecules have also been of considerable interest to theorists and spectroscopists owing to their high symmetry, planarity, and electronic delocalization. The physical properties of these square planar porphyrin-like molecules depend strongly on their chemical and geometric structure, providing an enormous opportunity for molecular design and control of properties by ligand substitution and ring symmetry modification.

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Despite their symmetric tetra- or octa-substituted anologs, unsymmetrical porphyrazines have received lesser attention, due to, in part, the difficulty in isolating the desired product from a mixed condensation of two different dinitrile derivatives. The development of the new methodology to synthesize phthalocyanines in which one of the fused benzo rings is replaced by another unsaturated moiety, has increased the numbers of investigations dramatically [10–14]. We have previously synthesized novel symmetric and unsymmetric phthalocyanines carrying macrocyclic substituents, alkylthio groups, or bulky groups on the periphery [15–21]. A consequence of incorporating sulphanyl functions on the periphery of these macrocycles has been the shift of the Q-band absorption to longer wavelengths which is preferred for a number of applications, such as in the case of IR absorbers, semiconductor lasers, and photosensitizers [22–24]. Also quaternizable aza-functions have provided products soluble in aqueous solutions over a wide range of *pH* values [25, 26].

This present paper describes the preparation of novel tribenzoporphyrazine structures carring both sulfanyl and quaternary ammonium functions on the periphery.

Results and Discussion

Three general methods exist for the preparation of unsymmetrical porphyrazines from two different dinitrile derivatives $A(CN)_2$ and $B(CN)_2$ as $M(pz(AB_3))$ structures: the polymer support route [27, 28], the subphthalocyanine route [29], and the statistical condensation route [10]. Here, for the synthesis of dimethyl-aminoethylthio-substituted tribenzoporphyrazine structures we preferred the statistical condensation route with bis(dimethylaminoethylthio)maleonitrile (**1**) and phthalonitrile (**2**) as the precursors.

Normally, a mixed cyclization is expected to yield all six porphyrazine structures that can result from the combination of the two dinitriles in the reaction mixture. Recently, *Hoffman* and co-workers [30] have described a new approach for the synthesis of unsymmetrical porphyrazines in which one of the benzo rings of phthalocyanines is replaced by a dithiomaleonitrile derivative to give only two porphyrinic compounds as the main products. This problem is avoided by using an excess of phthalonitrile (present in 15–25 fold excess) with a dithiomaleonitrile derivative to give only two porphyrinic products, insoluble Mg*Pc*, and a relatively soluble product composed of three phthalonitrile units and one maleonitrile derivative with the proper unsymmetric structure. Here, this method was used to synthesize unsymmetrical porphyrazines with the 2-dimethylaminoethylthio-maleonitrile group as the solublizing group. Thus, Mg tribenzoporphyrazine was prepared by the mixed condensation of bis(dimethylaminoethylthio)maleonitrile (**1**) with phthalonitrile (**2**) in 1:25 ratio using Mg butoxide as the template. This reaction gave the soluble, unsymmetrical Mg tribenzoporphyrazine **3** (10% yield), which had been designed to be easily separated from the insoluble Mg-phthalocyanine by-product. Further purification of the product was achieved by chromatography on silica gel. Demetallation of **3** was accomplished by trifluoroacetic acid to give the unsymmetrical metal-free porphyrazine **4**. Remetallation of the porphyrazine core with Zn(II) and Co(II) proceeded smoothly by treatment of the free base porphyrazine at reflux temperature with a small excess of the appropriate

metal acetate to yield **5** and **6**. The porphyrazines showed a rather low solubility in organic solvents when compared with octa-substituted porphyrazines and phthalo-cyanines carrying a similar substituent [31, 32]. Metal-free **4** and metallo porphyr-azines **5** and **6** are soluble in *THF* at a range of about $5–5.6\,mg\,cm^{-3}$.

When **3** was treated with methyl iodide in *THF*, the hygroscopic porphyrazine **7** with two quaternary ammonium groups was obtained. The novel compounds were characterised by IR, NMR, mass, and UV-Vis spectral data together with elemental analysis. The spectral data for all the new products were consistent with the assigned formulas and data for similar macrocycles [33–35].

In the IR spectrum of **3**, the CH vibrations of the dimethylaminoethylthio groups kept their places around $2940–2750\,cm^{-1}$, but as expected, the C≡N stretching vibrations of the starting materials **1** and **2** disappeared after porphyr-azine formation. The IR spectra of the metal-free derivative **4** and the porphyrazine complexes **5**, **6**, and **7** were very similar to **3** and did not show appreciable change by quaternization of the latter. In addition, for unsymmetrical metal-free porphyr-azine **4**, NH stretching vibrations of the inner core were observed at $\bar{\nu} = 3280\,cm^{-1}$. These protons are also well characterized by the ^{1}H NMR spectrum with a signal at $\delta = -3.5\,ppm$ as a consequence of the 18-π electron system of the porphyrazine ring. Also ^{1}H NMR spectroscopy played a key role in recognizing the unsymmetrically substituted porphyrazines **3–7**, with the resonances in the region $\delta = 2–4\,ppm$ being assigned to the methylene protons of the substituents. In the

1   **2**

3   **4**   **5**   **6**   **7**

$M = Mg^{2+}$ 2H Zn^{2+} Co^{2+}
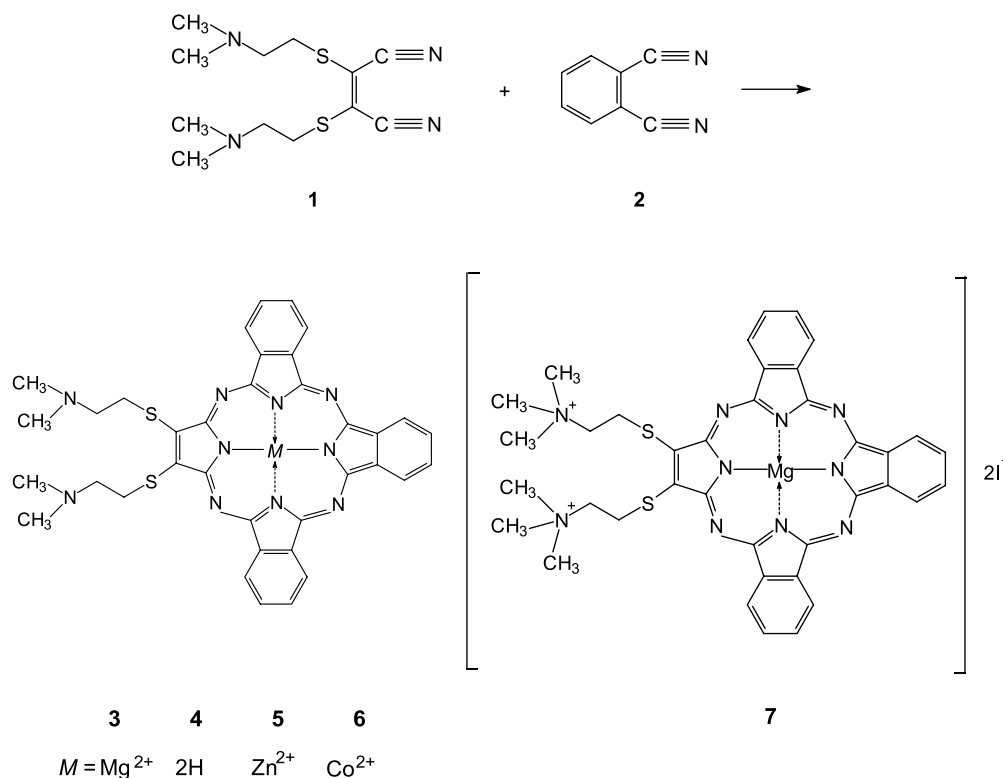
^{1}H NMR spectrum of **3**, the aromatic protons were observed between 8.44–7.29 ppm as a multiplet and the S–CH$_2$, N–CH$_2$, and CH$_3$ protons of the dimethylaminoethyl moiety were observed at 4.15 and 3.16 ppm as triplet and 2.23 ppm as singlet. In addition, the assignment of the product to a 3:1 combination of the reactants was made on the basis of elemental analysis and mass spectral results confirming the proposed structures. The molecular ion peaks at 670 and 727 were obtained by FAB for **4** and **6**.

Porphyrazines like phthalocyanines typically show an intense B (*Soret*) band below 400 nm and a Q band that has its principal absorption at 600 nm, with additional vibrations at shorter wave-lengths [36]. Also electronic spectra can be used in order to differentiate metal-free and metallo-porphyrazines. A single Q band in metallo-derivatives and its splitted form in their metal-free counterparts are characteristic [37]. A typical spectrum of the metal-free porphyrazine **4** in *THF* showed split Q bands at $\lambda = 654$ and 690 nm while the metallo-porphyrazines each gave an intense single band at $\lambda = 668$, 669, 655, and 664 nm for the corresponding compounds **3**, **5**, **6**, and **7**.

Experimental

IR spectra were recorded on a Mattson 1000 FTIR spectrometer using KBr pellets. UV-Vis spectra were measured on a UNICAM UV-Vis spectrophotometer. Elemental analyses were performed at the Instrumental Analysis Laboratory of TÜBİTAK Marmara Resarch Centre; result agreed well with calculated values. Proton NMR spectra were recorded on a Bruker 250 MHz spectrometer using *TMS* as internal standard. Mass spectra were recorded on a VG ZAB-SPEC spectrometer.

Bis(2-dimethylaminoethylthio)maleonitrile (**1**) was prepared according to Ref. [32]. All other reagents and solvents were of reagent-grade quality obtained from commercial suppliers. All solvents were dried and purified according to Ref. [38].

[2,3-Bis(2-dimethylaminoethylthio)tribenzoporphyrazinato]magnesium(II) (**3**, C$_{36}$H$_{32}$N$_{10}$S$_2$Mg)

Magnesium powder (0.828 g, 34.52 mmol) was added to 200 cm^3 of *n*-butanol and heated to reflux for 24 h. Once boiling, a small chip of I$_2$ was added to initiate the formation of a magnesium butoxide suspension. A mixture of bis(2-dimethylaminoethylthio)maleonitril (**1**) (0.754 g, 2.65 mmol) and phthalonitrile (**2**) (8.496 g, 66.37 mmol) was added to the solution and the mixture was heated for an additional 12 h. During this time the solution turned from an orange to brown and finally to blue-black. After the hot mixture was filtered, the remaining blue-black residue was refluxed with methanol and filtered off. The residue was taken up in CHCl$_3$ and filtered to remove the insoluble Mg(*pc*) formed as a by-product during the cyclization reaction. After concentration, the filtrate was purified by chromatography (silica gel, *Me*OH:*THF* = 1:20). Yield 0.182 g (10%); IR: $\bar{\nu} = 2940$–2750 (alkyl CH) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 2.23$ (s, 4CH$_3$), 3.16 (t, 2N–CH$_2$), 4.15 (t, 2S–CH$_2$), 7.29–8.44 (m, 12Ar-H) ppm; UV-Vis (THF): λ ($\varepsilon \cdot 10^{-4}$) = 668 (11.74), 639 (1.60), 604 (1.77), 345 (2.85) nm.

2,3-Bis(2-dimethylaminoethylthio)tribenzoporphyrazine (**4**, C$_{36}$H$_{34}$N$_{10}$S$_2$)

Crude **3** (0.5 g) was dissolved in 6 cm^3 of trifluoroacetic acid and stirred at room temperature for 3 h. The solution was poured into ice-H$_2$O and stirred. It was neutralized with aqueous NH$_3$ (25%) and precipitation was completed. The precipitate was filtered, washed first with H$_2$O, then with methanol,

and dried *in vacuo*. The solid product was extracted with *THF* in a *Soxhlet* for 24 h in order to separate the desired product from the insoluble metal-free phthalocyanine. After evaporation of the solvent a pure product was obtained by washing the residue with methanol and diethylether. Yield 0.106 g (22%); IR: $\bar{\nu} = 3280$ (NH), 2940–2750 (alkyl CH) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = -3.51$ (br. s, NH), 2.32 (s, 4CH$_3$), 3.28 (t, 2N-CH$_2$), 4.17 (t, 2S-CH$_2$), 7.26–8.45 (m, 12Ar-H) ppm; UV-Vis (*THF*): λ ($\varepsilon \cdot 10^{-4}$) = 690 (5.65), 654 (5.02), 636 (1.93), 594 (1.3), 338 (3.66) nm.

[2,3-Bis(2-dimethylaminoethylthio)tribenzoporphyrazinato]zinc(II) (**5**, C$_{36}$H$_{32}$N$_{10}$S$_2$Zn)

To a solution of 55 mg of Zn(CH$_3$COO)$_2$ (0.3 mmol) in 10 cm^3 of absolute ethanol a solution of 0.1 g of **4** (0.15 mmol) in 15 cm^3 of *THF* was added under N$_2$. The mixture was heated under reflux with stirring for 18 h. The crude product was filtered off and washed successively with H$_2$O, methanol, ethanol, and then dried under vacuum. Yield 0.085 g (78%); IR: $\bar{\nu} = 2990$–2870 (alkyl CH) cm^{-1}; UV-Vis (*DMF*): λ ($\varepsilon \cdot 10^{-4}$) = 669 (9.47), 604 (2.16), 344 (3.56) nm.

[2,3-Bis(2-dimethylaminoethylthio)tribenzoporphyrazinato]cobalt(II) (**6**, C$_{36}$H$_{32}$N$_{10}$S$_2$Co)

Prepared according to the procedure described for **5** starting from 0.15 g of **4** (0.22 mmol) and 0.078 g of Co(CH$_3$COO)$_2$ (0.44 mmol). Yield 0.105 g (65%); IR: $\bar{\nu} = 2970$–2840 (alkyl CH) cm^{-1}; UV-Vis (*THF*): λ ($\varepsilon \cdot 10^{-4}$) = 655 (6.19), 325 (5.86) nm.

[2,3-Bis(2-trimethylaminoethylthio)tribenzoporphyrazinatomagnesium]diiodide (**7**, C$_{38}$H$_{38}$N$_{10}$S$_2$I$_2$Mg)

Magnesium complex **3** (0.2 g, 0.29 mmol) was dissolved in 20 cm^3 of *THF* and 0.41 g of methyl iodide (2.9 mmol) were added. The mixture was stirred in the dark under N$_2$ at room temperature for 24 h. The blue precipitate was filtered off, washed with *THF*, then with diethylether, and dried under vacuum over P$_2$O$_5$. This porphyrazine was soluble in methanol, *DMSO*, and *DMF*, and slightly soluble in ethanol and water. Yield 0.155 g (55%); IR: $\bar{\nu} = 2980$–2775 (alkyl CH) cm^{-1}; UV-Vis (*DMSO*): λ ($\varepsilon \cdot 10^{-4}$) = 673 (9.63), 608 (1.57), 348 (3.12) nm.

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